DEVELOPMENT OF HIGHLY DISPERSED COAL LIQUEFACTION CATALYSTS

Toshimitsu Suzuki

Department of Chemical Engineering, Kansai University
Suita, OSAKA JAPAN 564

Key Words
Iron carbonyl, Coal liquefaction kinetics, Dispersed catalyst,

Introduction
Recently much attention has been focused on the highly dispersed catalyst for coal hydro-liquefaction.[1] We have been developing highly dispersed catalyst for coal liquefaction since 1981.[2] In 1951 Weller and Peripetz first reported that the distribution of the catalyst is very important for the high activity.[3] However, exact roles of coal liquefaction catalyst have not been well elucidated. Until now understandings of coal liquefaction catalyst involves many contradictory arguments.

Our understanding in coal liquefaction reaction mechanisms is as follows: Thermal scission of covalent bonding in coal macromolecular structure occur to give free radicals, followed by stabilization by a hydrogen abstraction either from hydrogen donor substances or a molecular hydrogen activated on a catalyst. This process is schematically represented in Scheme I.
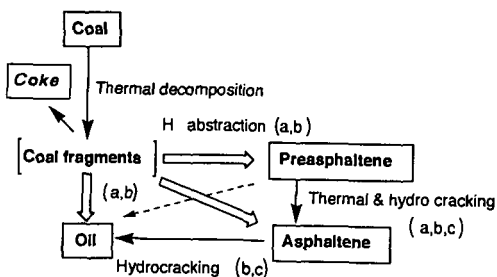
a) To keep good contact between catalyst and solid coal.
b) High activity toward hydrogen transfer in both coal fragment radicals and aromatic moiety.
c) High activity for cracking and hydrocracking of C-C bonds.
d) Cost of the catalyst should be low and recovery or recycle use of the catalyst should be easy.

From these view points, following four conditions would be required for the efficient coal liquefaction catalyst.
Among them (a) and (b) are the most significant characteristics required for the catalyst in the early stage of the coal liquefaction course shown in Scheme I.

A catalyst which fulfill all the requirement shown above cannot be found hitherto. Among many catalysts previously investigated, $ZnCl_2$ or $SnCl_2$ is superior in functions (b) and (c), on the other hand, iron is important in the cost of metal (d). Co-Mo and Ni-Mo catalyst employed for the hydrodesulfurization of petroleum fractions are extremely active in functions (b) and (c). However, such a supported catalyst is poor in contact between catalysts and coal (a) and in addition deactivation of catalyst is indispensable.

Scheme I Coal liquefaction scheme and functions of the catalyst required in the particular steps

In several processes involved in coal liquefaction, hydrogen transfer to coal fragment radicals is the most important path in order to obtain higher coal conversion. A certain amount of coal fragment

radicals exist in the solid coal matrix or appear as partially fused macromolecular structure of which mobility is restricted, at the early stage of the liquefaction. Under such conditions, contact between catalyst and solid coal is a very important factor to obtain higher coal conversion.

Previous attempts to use homogeneous transition metal complexes as a catalyst were not successful.[4] We have been noticed that iron carbonyl decomposes to give fine particles of iron metal at an elevated temperature. This prompts us to use iron carbonyl as a catalyst precursor of coal liquefaction. Iron carbonyl is freely soluble in a common organic solvent, therefore the catalyst precursor may penetrate into pore structures of coal at a lower temperature and above a decomposition temperature the precursor decomposes to a finely dispersed iron species on the solid coal. Thus good contact between the catalyst and solid coal could be attained.

Results of coal liquefaction with organometallic compounds[5,6]

Hydroliquefaction of coal with $Fe(CO)_5$ was carried out in a batch 50 mL micro autoclave under various reaction conditions. A 2.0 g of coal and 4.0 mL of vehicle oil (1-methylnaphthalene or tetralin) was charged with a certain amount of catalyst. The autoclave was heated to the desired reaction temperature and shaked. The reaction mixture was separated into preasphaltene asphaltene, and oil fractions.

The results of the liquefaction of Illinois No 6 coal (C:76.8 %) are summarized in Table I.[5] Since we have known that that $Fe(CO)_5$ exhibited higher catalytic effects than those of conventional iron catalyst previously reported, we wanted to carry out the liquefaction reaction at a higher reaction temperature in a short contact time. At an initial hydrogen pressure of 5.0 MPa, coal conversion was not high as expected (compare run 2 and 4). Increases in the initial hydrogen pressure to 8.0 MPa, remarkable increases in the coal conversion and oil yield were observed at a reaction time of only 20 min. At 480 °C a reaction time of 10 min is sufficient to obtain oil yield of 50 %. Conventional Fe_2O_3 catalyst afforded smaller coal conversion and oil yield of 43 % (see run 10). Even in a very short reaction time (10 min), conversions to THF soluble fraction were almost constant and very high (over 93 % in the temperature range of 425 to 480 °C). However, the asphaltene and oil yields increased with an increase in the reaction temperature. This indicates that conversion of THF soluble products to oil and asphaltene fractions can not be promoted with the iron catalysts at a lower temperature.

We have extended the use of iron carbonyl based catalyst to the liquefaction of Australian low rank coals (Yallourn C: 68.2 %, Wandoan C: 76.8 %). The results are summarized in Table II.[6] Much lower conversions were observed in the absence of the catalyst as compared to Illinois No6. coal. Use of $Fe(CO)_5$ increased conversions, but the increases are not significant as in the case of Illinois No.6 coal. Addition of one to two equivalent amount of sulfur to iron greatly enhanced the catalytic activity. Several iron carbonyl derivatives also enhanced coal conversion and oil yield markedly with sulfur.

The role of sulfur in the iron catalyst was examined by X-ray diffraction study of the residues from the liquefaction reaction.

Pyrrhotite has been proposed to be one of active species of iron-sulfur based catalyst by Montano.[7] In our case a liquefaction residue in $Fe(CO)_5$-S system clearly showed intense peaks attributed to $Fe_{1-x}S$ in the XRD pattern. On the other hand, that obtained in the absence of sulfur exhibited the peaks ascribed to Fe_3O_4. These findings indicate that active form of $Fe(CO)_5$ based catalyst is essentially the same as that of conventional iron oxide or iron sulfide based catalyst.

Further studies of an active form of $Fe(CO)_5$ based catalyst were done by using Mössbauer spectroscopy in the reaction with coal model copounds.[8] Mossbauer spectra of FeS_2 or Fe_2O_3-S based catalyst after a hydrocracking reaction of diphenylmethane exhibited clear sextet signals ascribed to $Fe_{1-x}S$. On the other hand, $Fe(CO)_5$-S based catalyst exhibited rather broad doublet signals in the center of the spectra, in addition to the sextet signals ascribed to $Fe_{1-x}S$. This absorption is probably attributed to highly dispersed paramgnetic iron species, so called superparamagnetic species.

Superiority in such a finely dispersed iron catalyst can be observed when hydrogenation of coal model compounds phenanthrene or pyrene were hydrogenated. Much higher conversion of condensed aromatic compounds to partially hydrogenated compounds were observed as compared to conventional

iron catalsysts such as Fe_2O_3 or FeS_2. On the hydrogenolysis of diphenylmethane or diphenylethane slightly higher activityies of $Fe(CO)_5$-S based catalyst was observed.

Kinetic studies of $Fe(CO)_5$ based catalysts[9]

Further investigation of the nature of $Fe(CO)_5$ based catalyst was carried out by kinetic treatment of coal liquefaction. A kinetic model used in our study is a combined parallel and consecutive reaction paths shown in Scheme II. Where first order rate constants were estimated by computer curve fitting methods. Typical results of curve fitting in the hydroliquefaction of Yallourn coal with $Fe(CO)_5$-S catalyst system is shown in Figure 1. The first order rate contestants summarized in Table III indicate that much larger values for k1,k4, and k5 in all the experiments shown here. Such tendency is more pronounced in the case of low rank coal (Yallourn). This indicates that direct depolymerization of this coal into asphaltene and oil fractions predominate over the consecutive path ways via preasphaltene intermediate. This seems to strongly reflect the chemical structure of low rank coal. Yallourn coal is thought to contains small amounts of condensed aromatic ring structure and to have large amounts of ether linkages, which would easily cleave thermally. Thus even at an early stage of the liquefaction smaller molecular weight fragment radicals would be formed. Most of them abstracts hydrogen from molecular hydrogen activated on the catalyst surface to give lower molecular weight products (asphaltene and oil).

Increase in the amount of catalyst markedly increased all the rate constants. As shown in Fig. 1, yields of preasphaltene and asphaltene reached maximum values at reaction times 10 and 20 min. respectively, and gradually decreased. Accordingly the yield of oil fraction increased with an increase in the reaction time. Among the rate constants k2 and k5 increased by about factor of 10 and 3 respectively with a 2.5 fold increase in the $Fe(CO)_5$. On the other hand k1, k4,and k5 increased by factors of about 3.

Effects of hydrogen partial pressure, reaction temperature, and coal rank are also discussed.

From these results the role of iron catalyst is ascribed to mainly activate molecular hydrogen and transfer hydrogen to coal fragment radicals in a non hydrogen donor solvent. In this stage fragment radicals tend to recombine, if the catalyst is not effective or the concentration is not sufficient. At the late stage of the liquefaction, condensed aromatic compounds in preasphaltene and asphaltene fractions are gradually hydrogenated to yield lighter oil fraction.

All these results clearly show superiority of the highly dispersed catalyst prepared from organo-tansition metal complexes. Combined with recent results, it is concluded that the catalyst used for coal hydroliquefaction played key functions for the hydrogen transfer reaction from gas phase to coal fragment radicals.

References

1. Fine Particle Catalyst Testing US DOE Advanced Research Liquefaction
2. Suzuki, T.; Yamada, O.; Fujita, K.; Takegami, Y.; Watanabe, Y. Chem. Lett., **1981**,1467-1468; Fuel, **1984**, *63*, 1706-1709.
3. Weller, S.; Peripetz, M. G. Ind. Eng. Chem., **1951**, *43*, 1243.
4. Cox, J. L.; Wilcox, W. A.; Roberts, G. L. *In Organic Chemistry of Coal*; Larsen, J. W. Ed.; ACS Symposium Series 77; American Chemical society; **1978**; pp 186-203
5. Suzuki, T.; Yamada, O.; Fujita, K.; Takegami, Y.; Watanabe, Y. Ind. Eng. Chem. Process Des. Dev., **1985**, *24*, 832-836.
6. Suzuki, T.; Yamada, O.; Takahashi, Y.; Watanabe, Y. Fuel Processing Tech. 1985, 10, 33
7. Montano, P. A.; Granoff, B. Fuel **1980**, *59*, 214-216, Bommannarar, A.; Montano, P. A. Fuel, **1982**, *61*, 1288-1290.
8. Suzuki, T.; Yamada, H.; Watanabe. Y. Energy Fuels, **1989**, *3*, 707-713.
9. Suzuki, T.; Ando, T.; Watanabe, Y. Energy Fuels,**1987**, *1*, 295-300.

Table 1 Hydroliquefaction of Illinois No.6 Coal Using Iron Pentacarbonyl[a]

run	catalyst [b]	H$_2$ MPa	Temp °C	Time min	Conv %	Gas %	Oil %	AS %	PA %	H$_2$ %
1	none	5.0	425	60	56.7	3.7	22.8	19.2	11.0	0.5
2	Fe(CO)$_5$	5.0	425	60	92.9	6.3	33.1	39.0	14.5	2.2
3	none	5.0	460	20	54.9	4.2	31.5	15.8	7.6	0.8
4	Fe(CO)$_5$	5.0	460	20	84.2	5.2	40.9	25.5	17.8	2.0
5	Fe(CO)$_5$	5.0	460	40	83.9	6.7	47.3	23.3	13.3	2.4
6	none	7.9	460	20	69.7	6.4	37.2	20.4	12.1	1.4
7	Fe(CO)$_5$	7.9	460	20	95.0	5.6	53.1	30.5	11.4	3.0
8	Fe(CO)$_5$[c]	7.9	460	20	94.8	4.6	56.2	26.2	10.2	2.7
9	none	7.9	480	10	61.2	5.3	34.9	16.2	10.1	1.2
10	Fe$_2$O$_3$	7.9	480	10	83.7	6.3	43.4	25.4	14.9	2.2
11	Fe(CO)$_5$	7.9	480	10	93.9	6.4	50.4	29.5	14.0	2.8

[a] Coal; 2.0 g, solvent, 1-methylnaphthalene; 4.0 mL. b Fe,0.4 mmol (1.1 wt % coal).
c Solvent ; Decalin

Table 2 Hydroliquefaction of Australian coals using iron-sulfur catalysts[a]

Run	Catalyst	Fe mmol	S	Conv.	Gas	Oil %	AS	PA	H$_2$
	Wandoan Coal								
1	none	0	0	48.6	7.8	22.3	12.6	5.9	0.2
2	Fe(CO)$_5$	1	0	85.2	6.9	35.5	21.0	21.8	1.8
3	Fe(CO)$_5$-S	1	1	94.4	9.5	48.6	24.8	11.5	2.8
4	Fe(CO)$_5$-S	2	2	94.7	7.5	47.3	27.5	12.4	2.6
5	Fe$_2$(CO)$_9$-S	1	1	92.7	8.1	47.7	25.8	11.1	2.6
6	Fe$_3$(CO)$_{12}$-S	1	1	94.8	7.9	46.2	27.7	12.8	2.9
7	Fe(acac)$_3$-S	1	1	81.6	12.0	23.7	25.2	20.7	2.4
8	Red mud-S	1	1	93.2	8.7	39.3	28.5	16.7	2.4
9	Fe$_2$S$_2$(CO)$_6$	1	1	93.3	8.0	42.1	29.8	13.4	3.0
	Yallourn Coal								
10	none	0	0	36.7	15.0	12.9	5.4	3.4	0.8
11	Fe(CO)$_5$	1	0	69.7	15.2	25.3	14.4	14.8	1.6
12	Fe(CO)$_5$	2	0	92.5	18.9	30.8	22.9	19.9	2.3
13	Fe(CO)$_5$-S	1	0.5	91.5	18.8	34.6	17.0	21.1	2.2
14	Fe(CO)$_5$-S	1	1	97.7	16.9	41.8	21.6	17.4	3.3
15	Fe(CO)$_5$-S	1	2	96.0	20.2	36.8	19.3	19.7	2.9

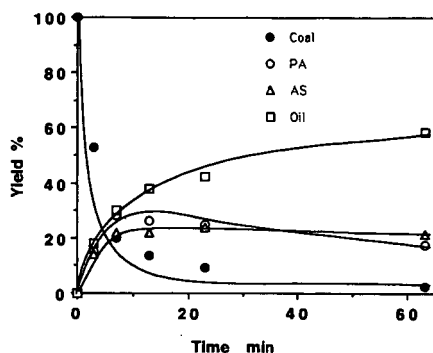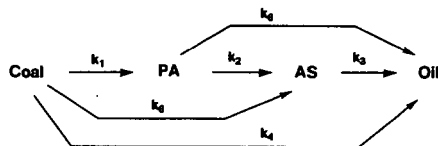a Coal; 2.0 g, 1-methylnaphthalene; 4.0 ml, H$_2$ pressure; 5.0 MPa, 425°C, 60 min.

Figure 1 Observed and simulated results of kinetics in
Yallourn coal hydroliquefaction
425 °C, Fe(CO)$_5$: 1.0 mmol, S: 1.0 mmol, PH$_2$=5.0 MPa

Scheme II   Kinetic model of liquefaction reaction

Table 3   Rate constants for hydroliquefaction of various coals with Fe(CO)$_5$ catalyst[a]

entry	Coal	catalyst mmol	PH$_2$ MPa	Conv.[b] %	rate constant, min^{-1}					
					k1	k2	k3	k4	k5	k6
1	YL	0.40	5.0	83.5	0.0213	0.0007	0.0007	0.0366	0.0178	0.0018
2	YL	1.00	5.0	97.7	0.0740	0.0078	0.0110	0.0760	0.0550	0.0049
3	YL	0.40	7.9	89.4	0.0380	0.0070	0.0062	0.0590	0.0380	0.0037
4	YL[c]	0.40	5.0	87.8	0.0230	0.0024	0.0	0.0340	0.0160	0.0
5	WD[c]	0.40	5.0	87.4	0.0700	0.0120	0.0100	0.0300	0.0330	0.0080
6	MK[c]	0.40	5.0	96.8	0.1300	0.0050	0.0038	0.0100	0.0700	0.0033

a Coal 2.0 g, 1-methylnaphthalene 4.0 mL, Temperature 425 °C,   b Conversion at 60 min
c at 400 °C